

Effect of Transition Metal Coordination on the Photophysical Properties of C₆₀. Triplet Formation and Lifetime in (η⁵-C₉H₇)Ir(CO)(η²-C₆₀)

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The unique carbon cluster C₆₀ shows remarkable photophysical properties.^{1–7} Laser excitation generates the excited singlet state, which undergoes very efficient intersystem crossing^{1b,4,7} to a long-lived triplet state. The lifetime of the singlet state was reported initially as 33 ps,³ but more recent measurements provide values near 1 ns.^{4–6} The triplet-state lifetime has been reported variously as 40 μs^{1a} and ≥280 μs⁵ in solution and as ca. 300 μs in a toluene glass.³ It is of interest to examine how these relatively long excited-state lifetimes are affected in derivatives of C₆₀, in particular, in 1:1 complexes with transition metal centers.⁸ In this paper we report the first measurements on the formation and lifetime of an electronic excited state of a metalated C₆₀ derivative.

The indenyliridium complex (η⁵-C₉H₇)Ir(CO)(η²-C₆₀),^{8a} [Ir–C₆₀], forms air-stable green solutions in noncoordinating organic solvents. The UV features of the electronic absorption spectrum of [Ir–C₆₀] are little changed from those of C₆₀ itself; however, the visible spectrum shows a well-defined new absorption band at 436 nm.^{8a} The position of this band does not change with solvent polarity (hexane, benzene, dichloromethane) or upon the addition of an electron to the C₆₀ ligand.⁹ These characteristics suggest that the 436-nm band is not due to an Ir-to-C₆₀ charge-transfer transition but rather arises from a transition largely centered on the C₆₀ ligand. One possibility is a relatively localized π–π* type transition involving the coordinated double bond, a transition derived from the HOMO–LUMO (h_u → t_{1u}) transitions that are symmetry forbidden in free C₆₀. In this regard, it is significant that a similar new band is seen in the recently reported spectrum of C₆₀O.¹⁰

The transient absorption spectrum of [Ir–C₆₀] shown in Figure 1 was recorded 50 ns after pulsed 388-nm irradiation of a nitrogen-purged toluene solution.¹¹ Three strong transient absorptions are observed at 420, 490, and 720 nm, very similar to those observed for C₆₀ itself.^{5,6,12} The same transient spectrum is obtained for [Ir–C₆₀] following excitation at 308 nm. The transient absorptions formed by laser irradiation decay to >90%,

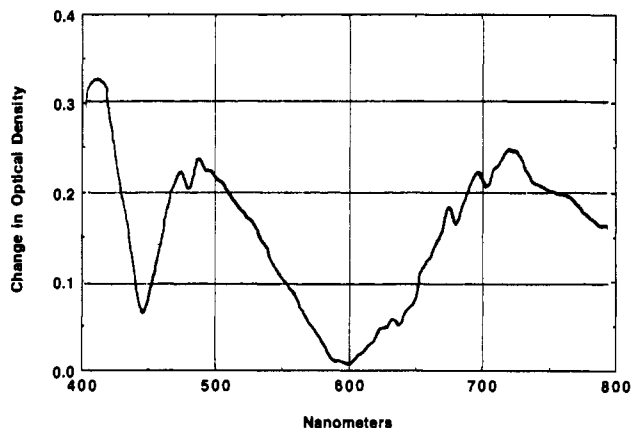


Figure 1. Transient absorption of [Ir–C₆₀] in toluene purged with N₂ (laser pump at 388 nm (20-ns width) with 50-ns delay; solution optical density 2.1 at 388 nm).

but there is a small component that does not decay over 100 μs. Nevertheless, no change in the absorption spectrum of the solution is observed after multiple laser flashes.¹³

The lifetime of excited [Ir–C₆₀] in nitrogen-purged and oxygen-saturated solutions was determined by monitoring the transient absorption at 720 nm. The data in Figure 2 show a first-order decay under both conditions, with lifetimes of 100 and 25 ns, respectively. Similar results are obtained when the transient absorption is monitored at 435 or 490 nm. Thus, these three transient absorption features are assigned to the same state, namely, “triplet” [Ir–C₆₀] (vide infra).

For comparison with the iridium complex, the triplet lifetime of free C₆₀ was measured under our conditions.¹¹ A solution of C₆₀ in dry benzene was degassed and irradiated at 388 nm with a 20-ns, 10-mJ pulse from a dye laser. The absorption spectrum of triplet C₆₀, recorded from 400 to 800 nm, was the same as that reported by previous workers.^{5,6,12} Lifetime measurements at 740 nm (3.2 mJ) showed apparent single-exponential decay, yielding a triplet lifetime of 29 ± 1.5 μs. However, the observed

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- Transient absorptions and kinetics of C₆₀ and [Ir–C₆₀] were measured on a Lambda Physik FL3002 laser system. A 20-ns pulse at 308 nm was generated directly by an XeCl excimer laser, and the pulse at 388 nm was generated by an excimer laser pumped BiBuQ dye laser. A perpendicular probe beam was obtained from a continuous or a flash Xe lamp and transmitted through appropriate cutoff filters. For the 740- and 720-nm probe beams, a RG 610 filter was used, and for the 505- and 490-nm probe beams, a Corning 3-73A filter was used. The probe beam sampled a volume element ca. 1.5 mm wide adjacent to the front window of the cuvette. Transient absorption spectra were recorded with a dual-diode array OMA analyzer, and kinetic data were obtained with a HP54111D transient digitizer. The [Ir–C₆₀] solutions had optical densities in 1-cm cells of ca. 2 at excitation wavelengths of 308 and 388 nm. Due to lower solubility, the C₆₀ samples had optical densities of ca. 0.3 at 388 nm.
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- A solution of [Ir–C₆₀] in dry benzene degassed by freeze-pump-thaw cycles was irradiated with 350-nm light in a Rayonet photoreactor at ca. 35 °C. There was no detectable change in the UV absorptions in 3 h, and only minor changes occurred after 15 h. However, the transient kinetics of irradiated solutions revealed a more significant change in the triplet lifetime. After 3-h irradiation, the decay was biexponential, and the slower rate component contributed more with increased irradiation time. The difference between steady-state and laser irradiation may be due to multiphoton effects in the latter case.

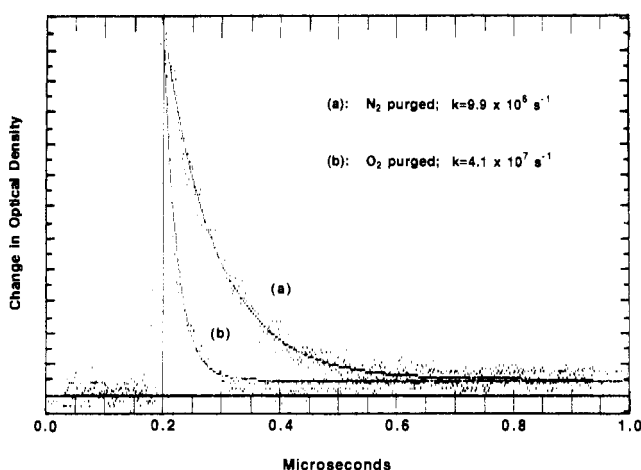


Figure 2. Transient kinetics of $[\text{Ir-C}_{60}]$ in toluene solution (pump beam, 388 nm; probe beam, 720 nm): (a) purged with N_2 ; (b) purged with O_2 .

lifetime depended on the power of the laser pulse, and extrapolation of the power dependence to zero gave a limiting experimental lifetime of $56 \pm 3 \mu\text{s}$. A similar study in benzene- d_6 yielded the same value ($60 \pm 3 \mu\text{s}$) within experimental error.¹⁴ Thus, the lifetime of triplet C_{60} is ca. 500 times longer than that of triplet $[\text{Ir-C}_{60}]$ under comparable circumstances.

We have attempted to determine the rate of formation of triplet $[\text{Ir-C}_{60}]$ by picosecond time scale spectroscopic techniques.¹⁵ Irradiation of a benzene solution of $[\text{Ir-C}_{60}]$ with an 18-ps laser pulse at 355 nm leads to the apparently instantaneous formation of the triplet state. For comparison, the rise time of triplet C_{60} measured under our conditions is $1.0 \pm 0.1 \text{ ns}$, a value which is compatible with other recent measurements.⁴⁻⁶ These findings indicate that the rate of intersystem crossing for singlet excited $[\text{Ir-C}_{60}]$ is at least 50 times greater than for C_{60} itself, an effect attributable to enhanced spin-orbit coupling in the presence of the metal atom.

The observed effect of oxygen on the lifetime of triplet $[\text{Ir-C}_{60}]$ suggested the formation of singlet oxygen by energy transfer.^{1,16} This has been probed directly by examining the conversion of tetramethylethylene (TME) to its characteristic allylic hydroperoxide under controlled conditions.¹⁷ Irradiation of O_2 -saturated benzene solutions containing TME and either $[\text{Ir-C}_{60}]$, C_{60} , or tetraphenylporphyrin (TPP) as sensitizers gave the expected hydroperoxide.¹⁸ Under identical conditions, C_{60} ¹ and TPP¹⁹ are equally effective sensitizers of singlet oxygen, but

$[\text{Ir-C}_{60}]$ produces only ca. 60% as much hydroperoxide, a value consistent with the oxygen-quenching efficiency shown by laser spectroscopy.²⁰

We conclude that the transient species detected by laser irradiation of $[\text{Ir-C}_{60}]$ should be assigned as a triplet excited state on the basis of its facile energy transfer to oxygen. This property has been observed frequently for triplet MLCT excited states of organometallic complexes;²¹ e.g., the excited-state lifetime of $\text{W}(\text{CO})_5\text{L}$ (L = 4-cyanopyridine) in hydrocarbon solution at room temperature drops from 250 ns under argon to 40 ns under oxygen.²² The orbital character of the $[\text{Ir-C}_{60}]$ excited state is less clear, however. The close similarity of the transient absorption features to those of C_{60} suggest a state based on an intraligand (IL) transition. However, the 500-fold diminution in excited-state lifetime is more dramatic than might be expected; the lifetime of the $n-\pi^*$ triplet state of 3-benzoylpyridine is reduced only 4-fold when N-bound to a rhenium center,²³ and the lifetime of the excited singlet state of rubrene is essentially unaffected in a compound with four π -complexed Cp^*Ru^+ centers.²⁴ The absorption features observed for triplet $[\text{Ir-C}_{60}]$ are not incompatible with an Ir-to- C_{60} MLCT state, and the measured lifetime is comparable with lifetimes determined for triplet MLCT states of third-row transition metal complexes of substituted pyridine and related ligands,²¹ e.g., $\text{W}(\text{CO})_5\text{L}$,²² $\text{Re}(\text{CO})_3\text{Cl}(\text{L-L})$,²⁵ and $\text{CpRe}(\text{CO})_2\text{L}$.²⁶ Finally, it is possible that two closely energetic states may both contribute to observed photophysical and photochemical behavior.^{21,27-29} Further work will be necessary to answer these questions regarding electronically excited $[\text{Ir-C}_{60}]$.

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(15) The picosecond transient absorption spectra were obtained by the pump-probe method using laser pulses (18-ps fwhm at 5-Hz repetition rate) from an actively-passively mode-locked Nd:YAG laser (Quantel, Model YG 501-C). The samples were excited by the third-harmonic 355-nm beam. The white light continuum, which was the probe beam, was generated by passing the residual fundamental beam (1064 nm) into a cell containing a $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture. The probe beam was split into two parts, one part nearly collinearly overlapping with the excitation beam at the sample and the other passing through the unirradiated portion of the sample. The two beams were then focused onto a slit of a spectrograph (Jobin-Yvon) and then to an intensified dual-diode array (ST-100, Princeton Instruments, Inc.). The probe beam was delayed by corner cube prisms on a translational stage controlled by a microcomputer. The sample was flowed to avoid multiple exposure.

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(18) A 0.1 M solution of TME (>98%, 3.45 g) in purified benzene (40 mL) was divided equally into four Pyrex test tubes. To two of the tubes were added small, equal amounts of $[\text{Ir-C}_{60}]$. To the other two tubes were added small amounts of TPP and C_{60} , respectively. The concentrations of the sensitizers were adjusted such that all light impinging on the samples would be absorbed (optical densities of ca. 4-6 in 1-cm cells). One of the tubes containing $[\text{Ir-C}_{60}]$ was wrapped with aluminum foil as a control. The tubes were placed in a Rayonet photoreactor containing 16 350-nm lamps. Oxygen was passed through a $\text{CaSO}_4/4\text{-\AA}$ molecular sieve/ CaSO_4 drying column and then slowly and continuously bubbled through the solutions. The temperature was controlled below 10 °C during irradiation by cooling with water. After 30 min of irradiation, the yield of hydroperoxide was determined by gas chromatography, by using dioxane as an internal standard.

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(20) The efficiency of oxygen quenching can be calculated as follows. If the lifetime of $[\text{Ir-C}_{60}]^*$ in the absence of O_2 is k_0^{-1} , then in the presence of O_2 it is $(k_0 + k_{\text{O}_2}[\text{O}_2])^{-1}$. In this case, one calculates that $k_{\text{O}_2}[\text{O}_2] = 3k_0$, so the quantum yield of quenching is $\Phi_q = (k_{\text{O}_2}[\text{O}_2]) / (k_{\text{O}_2}[\text{O}_2] + k_0)^{-1} = 0.75$. Note that $k_{\text{O}_2} \approx 3 \times 10^9 \text{ s}^{-1}$, if $[\text{O}_2] \approx 0.01 \text{ M}$. We thank a reviewer for comments in this regard.

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